Generalized Relation Between Surface Tension and Viscosity: a Study on Pure and Mixed n-alkanes[1]

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Abstract

A generalized relation is presented to correlate liquid-vapor surface tension with viscosity, both for pure compounds and mixtures.

Plots of different data sets verify that the natural logarithm of the surface tension is linear with the reciprocal viscosity, with slope dependent on the molecular weight and constant intercept for n-alkanes with chain length greater than n-$C_{10}H_{22}$. For these, the value of the intercept can be related to the surface tension at the temperature of homogeneous nucleation, where the reciprocal viscosity tends to zero.

The relations found for the slope and intercept of pure components are also shown to be valid for mixtures, so that only a viscosity (or surface tension) value is required to calculate a surface tension (or viscosity).

Some distillation cuts from crude oils of different origins were also presented. Although the linear relation is still valid, the proposed correlations for the slope and intercept of n-alkanes cannot be used, confirming that mixing rules and family-specific correlations are required for fluids containing components of different families.

The results presented on this work show how bulk transport and equilibrium surface properties can be interrelated.

1. Introduction

Thermophysical properties are required both for engineering and product design. Since experimental measurements are often unavailable, expensive and time-consuming, models are regularly used.

For the chemical engineer, surface tension not only determines the quality of many of the products resulting from different industries such as those producing coatings, paints, detergents, cosmetics and agrochemicals, but also affects some important steps in the production process: catalysis, adsorption, distillation and extraction are some of the examples. The importance of viscosity is also well known. All equations expressing the flow of fluids contain this property and several product characteristics can be largely determined by its magnitude. Lubricants and paints are examples of products for which the viscosity is one of the key properties.

In this work, n-alkane surface tension and viscosity data were used to evaluate a linear relation between the natural logarithm of the surface tension and the reciprocal viscosity, first proposed by Pelofsky [1]. The interest in these relations follows from the possibility of obtaining one of these properties from measurements on the other, thus overcoming data deficiency. These relations can also be used to test the validity of measured data, since deviations can be ascribed to experimental errors.

It will be shown that this relation holds both for pure compounds and mixtures of n-alkanes. Since most of the available n-alkane data is from the lowest members of the

series, this paper will be mostly focused on the heavier members and some of their mixtures with lighter components (asymmetric mixtures). Results on petroleum distillation cuts, representative of real systems will also be discussed.

2. Background

Following several attempts to relate surface tension with viscosity, Pelofsky [1] presented in 1966 a linear relation between these two thermophysical properties:

$$\ln \sigma = \ln A + \frac{B}{\eta} \tag{1}$$

where A and B are constants, σ is the surface tension, and η the viscosity. According to Pelofsky [1], this empirical relation can be applied for both organic and inorganic phases of pure and mixed components. Several fluids were shown to follow these relations: n-alkanes in the range $n-C_2H_6-n-C_6H_{14}$, benzene, toluene, xylenes, phenol and other aromatics, n-alcohols in the range $CH_3OH - C_4H_9OH$, ketones, water and some aqueous solutions.

Latter, Schonhorn [2] introduced a correction in the second term of the right-hand side of Eq. 1 to fulfil the requirement that at the critical point surface tension goes to zero, while viscosity tends to a small, but constant value:

$$\ln \sigma = \ln A + \frac{B}{\eta_l - \eta_v} \tag{2}$$

where subscripts l and v stand for the liquid and vapor phase property, respectively. This relation was successfully applied for pure metals like sodium and potassium, salts such as KBr, NaBr and NaCl, n-decane, argon, benzene, water, CCl_4 and polyethylene.

In his work, Schonhorn [2] related $ln A$ with σ_N, the surface tension at T_N, the temperature of homogeneous nucleation, that is, the temperature were clusters start to form spontaneously. At this temperature, the reciprocal viscosity tends to zero and thus, $\sigma = A$. Both in the works from Pelofsky [1] and Shonhorn [2] no physical meaning has been given to the slope, B, although Pelofsky has used a functional of the molecular weight to correlate this constant for members of the same family.

3.Results and Discussion

Several thermophysical properties from pure, binary and ternary mixtures of n-alkanes have been reported on literature as a result of a broader project involving measurement and modelling of asymmetric n-alkane systems [3-7]. These data, together with other pure component data [8, 9] will be used for the purposes of this work. Since the literature information for surface tension is considerably smaller than that available for viscosity, surface tension will limit the temperature range of this study. For the same reason, no pressure effect will be considered at this point.

Following the work from Pelofsky [1], later re-evaluated by Schonhorn [2] and Pedersen *et al* [10], in this paper several pure and mixed n-alkanes were assessed. Since most of the available data has been taken far from the critical point, where the vapor phase viscosity is small compared to that of the liquid phase, we can drop the correction introduced in Eq. 2 and use Pelofsky's approach (Eq. 1). With this approach, although an incorrect description of the surface tension is obtained close to the critical point, no need for information on the vapor phase viscosity is required, and the formalism of Eq. 1 can be kept very simple and accurate, far from the critical point, while using a minimum amount of experimental data.

3.1. Pure components

In Fig. 1, the linear relation is verified for some of the studied n-alkanes, n-C_6H_{14} up to n-$C_{20}H_{42}$. The same trend below n-hexane was also verified in this work and has already been shown by Pelofsky [1]. In these plots, only two points in 163 happened to be outside the linear relation, but these were also found to be outliers in the surface tension or viscosity plots as a function of temperature. Thus, if a set of values is found to be away from the linear plot, that may indicate incorrect viscosity or surface tension measurements.
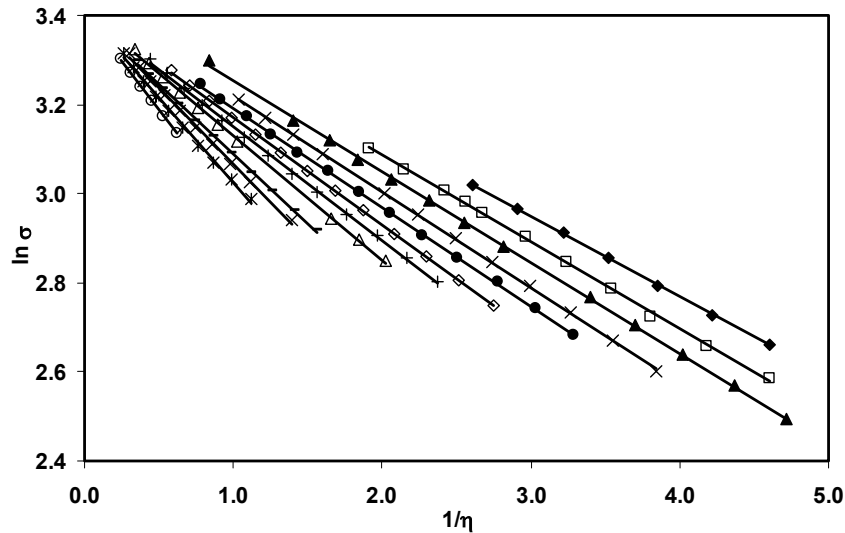
Fig. 1: Plots of ln σ as a function of reciprocal viscosity, 1/η for several pure n-alkanes: ◆, n-C_6H_{14}, □, n-C_7H_{16}, ▲ n-C_8H_{18}, x, n-C_9H_{20}, ●, n-$C_{10}H_{22}$, ◊, n-$C_{11}H_{24}$, +, n-$C_{12}H_{26}$, Δ, n-$C_{13}H_{28}$, -, n-$C_{15}H_{32}$, x, n-$C_{16}H_{34}$, *, n-$C_{18}H_{38}$, ○, n-$C_{20}H_{42}$.

As can be seen from Fig. 1 and Table 1, *ln A* tends to a value close to 3.41 as the chain length of the n-alkane increases. This corresponds, in Fig. 2, to a value of $\sigma_N = A$ of 30.2 mN.m^{-1}, which agrees quite closely with 31.6 mN.m^{-1}, reported by Shonhorn for polyethylene [2]. Below n-decane the values of ln A (and σ_N) seem to vary linearly with the chain length. The exception is methane, which although following the linear trend, present values that significantly deviate from linearity. For the other n-alkanes, up to n-C_9H_{20}, the following correlations can be used to obtain the value of *ln A*:

$$\ln A = 3.6314 - 0.0224 \times n \tag{3}$$

where n is the chain length of the n-alkane, C_nH_{2n+2}. If, instead, the molecular weight (MW) is used in the correlation, the following relation results:

$$\ln A = 3.6314 - 1.558 \times 10^{-3} \times MW \tag{4}$$

Table 1: Least squares fit for n-alkanes, and corresponding σ_N and T_N values.

n-alkane	B	ln A	$\sigma_N/mN.m^{-1}$	calc. T_N/K	T range/K
CH_4	-0.0922	3.35			93.15-163.15
C_2H_6	-0.138	3.60			133.15-193.15
C_3H_8	-0.162	3.55			203.15-263.15
$n-C_4H_{10}$	-0.174	3.54	34.5	124.8	233.15-293.15
$n-C_5H_{12}$	-0.166	3.52	33.8	148.3	233.15-293.15
$n-C_6H_{14}$	-0.180	3.49	32.8	164.0	273.15-333.15
$n-C_7H_{16}$	-0.194	3.48	32.3	181.0	273.15-363.15
$n-C_8H_{18}$	-0.204	3.46	31.7	198.5	243.15-393.15
$n-C_9H_{20}$	-0.215	3.43	31.0	213.5	273.15-393.15
$n-C_{10}H_{22}$	-0.222	3.41	30.4	227.3	273.15-393.15
$n-C_{11}H_{24}$	-0.241	3.41	30.3	234.5	273.15-393.15
$n-C_{12}H_{26}$	-0.256	3.41	30.1	242.8	273.15-393.15
$n-C_{13}H_{28}$	-0.279	3.41	30.2	247.1	273.15-393.15
$n-C_{14}H_{30}$	-0.297	3.41	30.1	255.0	283.15-393.15
$n-C_{15}H_{32}$	-0.312	3.40	30.0	262.0	293.15-393.15
$n-C_{16}H_{34}$	-0.341	3.41	30.2	266.1	293.15-393.15
$n-C_{17}H_{36}$	-0.363	3.41	30.2	270.1	293.15-393.15
$n-C_{18}H_{38}$	-0.380	3.41	30.1	274.1	303.15-393.15
$n-C_{19}H_{40}$	-0.388	3.39	29.8	280.1	313.15-393.15
$n-C_{20}H_{42}$	-0.447	3.41	30.3	278.8	313.15-393.15

From the intercept values reported in Table 1, and considering that for n-alkanes with chain length above $n-C_4H_{10}$ the viscosity term (B/η) in Eq.1 can be neglected close to the formation of the solid phase, temperatures corresponding to these surface tensions were calculated using correlations of experimental data. These temperatures are reported on Table 1 under the *calc. T_N* column. If compared with literature melting points [11] it can be recognized that these values fall systematically below the melting temperatures, with values of reduced undercooling, $\Delta T_r = (T_{fus} - T_N)/T_{fus}$ that agree with those known for the n-alkanes [12]. It can thus be concluded, following Schonhorn [2], that the value of A corresponds to the surface tension of the fluid at the temperature of homogeneous nucleation (T_N), and that this is constant for chain lengths higher than $n-C_{10}H_{22}$.
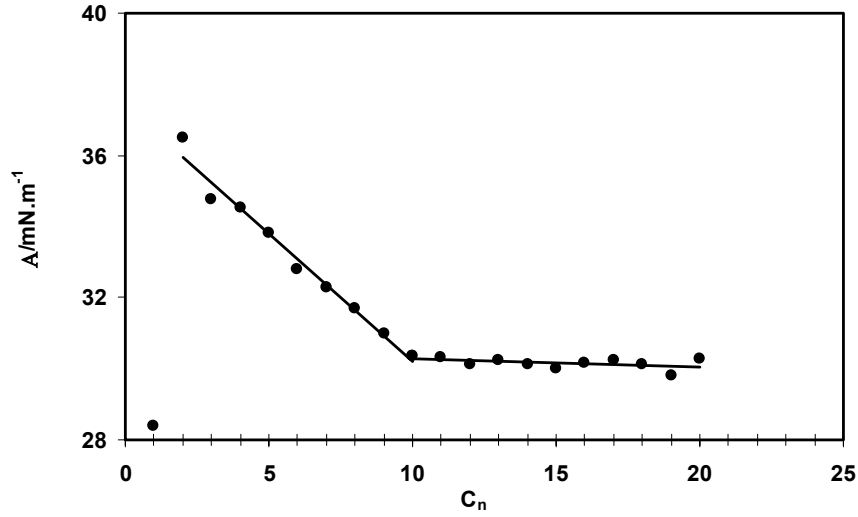
For the intercepts the same separation seems appropriate, as can be seen from Fig. 3. Below n-decane one linear trend can be assumed, where methane is again not included, Eqs. 5-6. Above n-decane another linear trend can be considered, Eqs. 7-8.

$$n<10, \qquad B = -0.1253 - 9.798 \times 10^{-3} \times n \qquad (5)$$
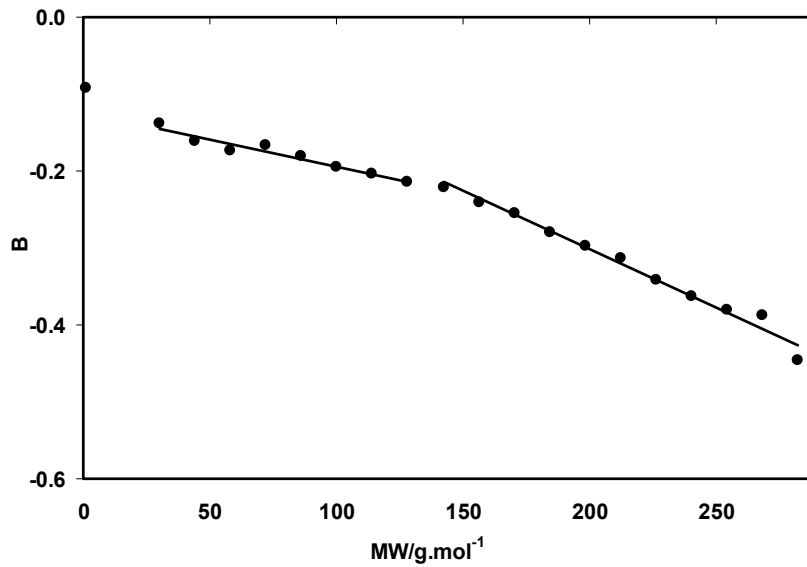
$$B = -0.1253 - 6.826 \times 10^{-3} \times MW \qquad (6)$$

$$n \geq 10 \qquad B = -2.135 \times 10^{-2} \times n \qquad (7)$$

$$B = -1.508 \times 10^{-3} \times MW \qquad (8)$$

Fig. 2: Plots of A as a function of chain length of the n-alkane.


Fig. 3: Plots of B as a function of MW.

In his work, Pelofsky [1] proposed to correlate the value of *B*, as a function of the molecular weight and thermal conductivity. Since that would introduce an additional variable in these relations, reducing its predictive ability, in this work, only the molecular weight of the n-alkane is used to correlate this parameter. The interest in using the molecular weight as a correlating variable, follows from the possibility of

applying this relation to more complex systems, for which compositional analysis are difficult to obtain and properties other than the molecular weight, boiling point or specific gravity, may be inaccessible as is the case for most of the petroleum fluids.

3.2. Synthetic mixtures

Following the results presented in the previous section, Eq. 1 was also evaluated for mixtures, namely asymmetric mixtures containing two or three n-alkanes. In Fig. 4 plots of ln σ as a function of $1/\eta$ for the mixture $n-C_{10}H_{22} + n-C_{20}H_{42}$ are presented at five different compositions. The linear trend is clearly evident, and again, the value of the intercept seems to converge.
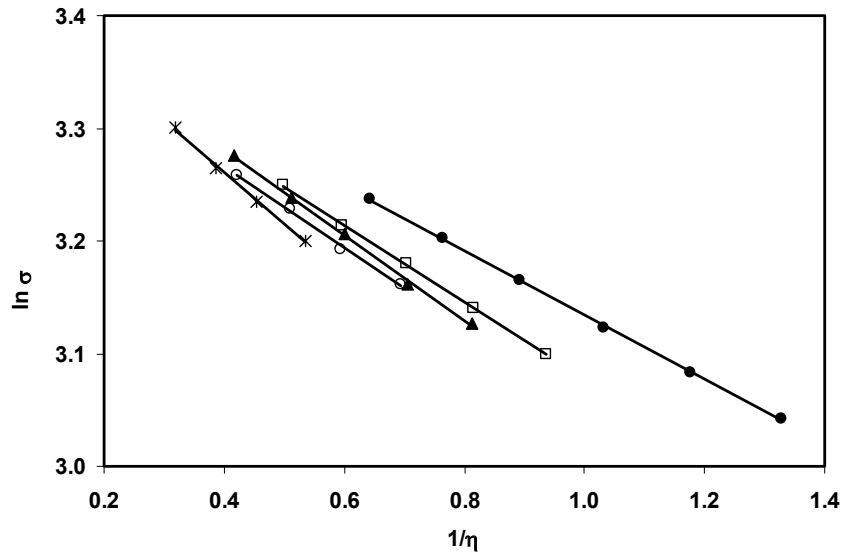
Fig. 4: ln σ as a function of $1/\eta$ for $n-C_{10}H_{22}$ (1) + $n-C_{20}H_{42}$ (2): ●, x(2)=0.2, □, x(2)=0.4, ▲, x(2)=0.5, ○, x(2)=0.6, *, x(2)=0.8.

Results of least-squares fits for systems of n-decane ($n-C_{10}H_{22}$) and n-hexadecane ($n-C_{16}H_{34}$) mixed with n-eicosane ($n-C_{20}H_{42}$), n-docosane ($n-C_{22}H_{46}$) and n-tetracosane ($n-C_{24}H_{50}$) are presented on Table 2. Viscosities and surface tensions, reported elsewhere [3, 4, 5, 7], where taken from 293.15 K (or above the melting point) up to 343.15 K.

All these mixtures have average chain lengths, ($n = \sum x_i \times n_i$) above 10, so from the conclusions of section 3.1, they may have the same intercept. In fact, from Table 2 one can check that the values of $ln\ A$ fall within a very short interval [3.38-3.43], with an average of 3.41, the same established previously for the pure components. Thus, in terms of intercept, a constant value of 3.41 applies also for mixtures with n ≥ 10. This can be confirmed in Fig. 5 for the mixtures reported on Table 2, were A is plotted as a function of the average chain length.

To verify that the slopes can also be calculated using the same equations as for the pure fluids, Fig. 6 was plotted using the B values reported on Table 2. A least-squares fit for the best linear equation gave a slope of -1.629×10^{-3}, which agrees within 6.6 % with -1.508×10^{-3}, reported on Eq. 8. Considering the dispersion of values on Fig. 6,

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Eq. 8 was considered to be also valid for mixtures. To check this assumption, Eq. 8 together with ln A= 3.41 were used to estimate surface tensions from viscosities and viscosities from surface tensions for mixtures of n-alkanes. Results are reported on Table 3.

Table 2: Least-squares fit for some n-alkane mixtures

Mixture	x(1)	x(2)	ln A	B	T range/K
	0.80	0.20	3.42	-0.285	293.15-343.15
	0.60	0.40	3.42	-0.340	303.15-343.15
n-$C_{10}H_{22}$(1)+n-$C_{20}H_{42}$(2)	0.50	0.50	3.43	-0.375	303.15-343.15
	0.40	0.60	3.42	-0.380	313.15-343.15
	0.20	0.80	3.44	-0.458	313.15-343.15
	0.60	0.40	3.39	-0.338	313.15-343.15
n-$C_{10}H_{22}$(1)+n-$C_{22}H_{46}$(2)	0.40	0.60	3.43	-0.452	313.15-343.15
	0.20	0.80	3.39	-0.349	323.15-343.15
	0.80	0.20	3.40	-0.325	313.15-343.15
n-$C_{10}H_{22}$(1)+n-$C_{24}H_{50}$(2)	0.60	0.40	3.40	-0.402	323.15-343.15
	0.50	0.50	3.41	-0.451	323.15-343.15
	0.80	0.10	3.38	-0.264	313.15-343.15
n-$C_{10}H_{22}$(1)+n-$C_{20}H_{42}$(2)+n-$C_{24}H_{50}$(3)	0.60	0.20	3.38	-0.337	313.15-343.15
	0.50	0.25	3.37	-0.329	313.15-343.15
n-$C_{20}H_{42}$(1)+n-$C_{24}H_{50}$(2)	0.50	0.50	3.42	-0.490	323.15-343.15
	0.80	0.20	3.43	-0.377	303.15-343.15
	0.60	0.40	3.43	-0.399	303.15-343.15
n-$C_{16}H_{34}$(1)+n-$C_{20}H_{42}$(2)	0.50	0.50	3.42	-0.374	313.15-343.15
	0.40	0.60	3.43	-0.418	313.15-343.15
	0.20	0.80	3.43	-0.431	313.15-343.15
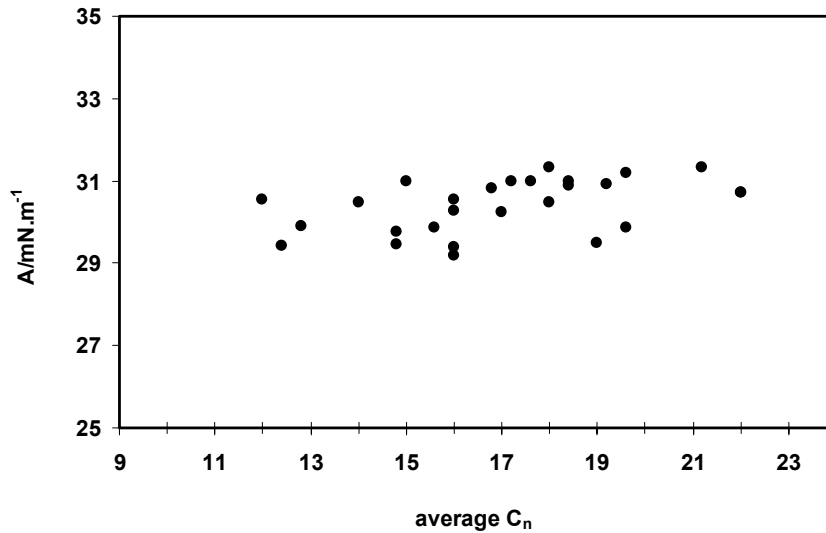
Fig. 5: Plots of A for n-alkane mixtures as a function of average chain length.
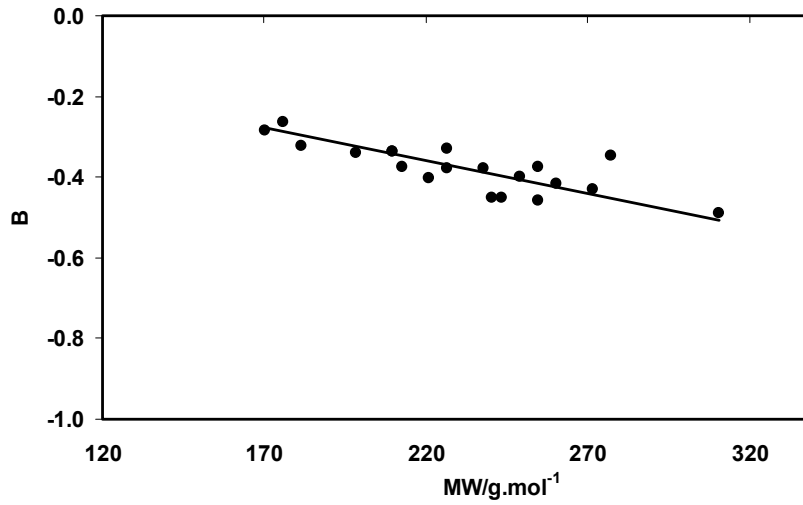
Fig. 6: Plots of B for n-alkane mixtures as a function of average molecular weight.

Table 3: Estimation of mixture surface tension or viscosity from Eq. 1 using *ln A*=3.41 and Eq. 8 for *B*.

| Mixture	Surf. tension, % AAD[a]	Viscosity, % AAD[a]
n-$C_{10}H_{22}$+n-$C_{20}H_{42}$	1.2	5.2
n-$C_{10}H_{22}$+n-$C_{22}H_{46}$	1.8	8.4
n-$C_{10}H_{22}$+n-$C_{24}H_{50}$	3.8	16.6
n-$C_{10}H_{22}$+n-$C_{20}H_{42}$+n-$C_{24}H_{50}$	2.7	11.6
n-C_7H_{16}+n-$C_{20}H_{42}$	7.8	26.2
n-C_7H_{16}+n-$C_{22}H_{46}$	8.5	29.2
n-C_7H_{16}+n-$C_{20}H_{42}$+n-$C_{24}H_{50}$	7.3	22.6
n-$C_{16}H_{34}$+n-$C_{20}H_{42}$	1.4	10.5
Average	3.2	13.1

$$ ^a\% \; AAD = \frac{1}{m} \sum_m \frac{|estimated - exp\,erimental|}{exp\,erimental} \times 100 $$

As can be seen from Table 3, very good surface tension estimation is obtained using Eqs. 1 and 8, with the maximum average deviations found for the most asymmetric mixtures. The same trend was found for the estimated viscosities, but higher deviations are observed, ranging from 5 % up to 29 % with an average of 13 %. It can thus be concluded that for the studied asymmetric n-alkane mixtures, Eq. 1 returns better estimates of surface tension from viscosity, than viscosity estimates from surface tension.

The results obtained for the surface tension open an opportunity to estimate this property at high pressure, for which the available experimental data are scarce and measurements harder to perform.

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3.3 Real Systems

In order to check the extension of this simple model to real fluids, three petroleum distillation cuts of different origins were selected for evaluation [13]. Plots of ln σ as a function of 1/η are shown on Fig. 7, and least-squares constants reported on Table 4. It can be confirmed that Eq. 1 continues to be valid, even for multicomponent fluids containing components from different families, as already demonstrated in a previous work by Pedersen et al. [10].
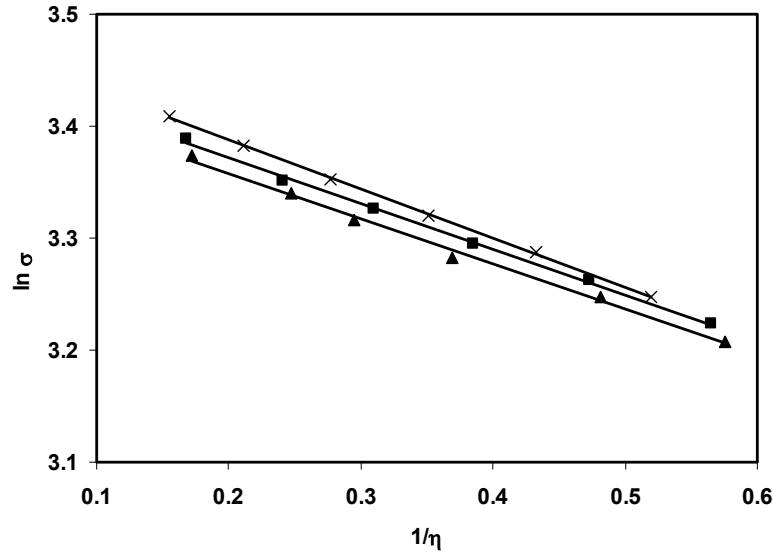
Fig. 7: ln σ as a function of 1/η for petroleum distillation cuts: ×, Troll, ■, Brent, ▲, Sahara Blend.

Molecular weight and n-alkane content, as reported elsewhere [13], are also included on Table 4. This time, both the intercept and slope are dependent on composition, and thus, the approach used before for pure and mixed n-alkanes cannot be implemented without the use of mixing rules.

Table 4: Least-squares fit for petroleum distillation cuts

Distillation cut	MW/g.mol^{-1}	% n-alkanes	ln A	B
Troll	231.7	9.79	3.48	-0.438
Brent	222.8	19.95	3.45	-0.408
Sahara Blend	235.8	21.17	3.44	-0.404

Pedersen *et al.* proposed a mixing rule [10] to use these relations for petroleum fluids. Composition in terms of a PNA (Paraffins-Naphtenes-Aromatics) distribution is required. Unfortunately, for the distillation cuts presented in this work, no PNA distribution was determined, and thus, the evaluation of this model for the reported distillation cuts is not possible.

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Conclusions

A linear relation between the natural logarithm of the surface tension and the reciprocal viscosity was found to be valid for pure n-alkanes, some of their binary and ternary mixtures and for petroleum distillation cuts of different n-alkane content.

The intercept can be linked with the surface tension at the temperature of homogeneous nucleation, where the reciprocal viscosity approaches zero. For n-alkanes with chain length higher than n-$C_{10}H_{22}$ this value is constant. Below n-$C_{10}H_{22}$, a linear correlation can be used for the calculation.

For the slope, two correlations where proposed: one for fluids with chain length higher than n-$C_{10}H_{22}$, and other for fluids with chain length smaller than n-$C_{10}H_{22}$.

Methane is not included in all of the proposed correlations, since its behaviour falls outside that observed for the other n-alkanes.

Some heavier and asymmetric n-alkane mixtures were evaluated for the extension of the proposed relation. Linearity was again observed, and interestingly, intercepts equal to those of the same chain length pure components were found. The same happened with the slopes that could be calculated from an equation obtained for the pure components. Using the equivalent pure component slopes and intercepts, very good surface tension estimates where obtained from viscosity data. If viscosity is to be obtained from surface tension larger errors shall be expected.

Finally, some petroleum distillation cuts of different origins where shown to follow the presented linear relation, but, as expected, the correlating equations presented before where not applicable, since these contain components other than n-alkanes.

List of symbols

A – constant calculated from least-squares fit.

B - constant from least-squares fit.

m – number of data points.

MW – molecular weight/ g.mol^{-1}.

n – chain length of n-alkane, C_nH_{2n+2}.

T – temperature/K.

x – mole fraction.

% AAD – average of % absolute deviations.

Greek letters

η – viscosity/mPa·s.

σ – surface tension/mN.m^{-1}.

Subscripts

    fus. – melting point.

    i – pure component.

    l – liquid phase property.

    N – homogeneous nucleation.

    v – vapor phase property.

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